



Sedimentary records of non-Aroclor and Aroclor PCB mixtures in the Great Lakes

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ABSTRACT

Three sediment cores from Lake Ontario, Lake Erie and Indiana Harbor Ship Canal were collected, segmented and analyzed for Aroclor and non-Aroclor polychlorinated biphenyl congeners (PCBs). PCBs associated with the commercially produced Aroclor mixtures 1248 and 1254 dominate the sediment signal and the sum of all congeners (Σ PCB) peaks in concentration and accumulation around 1970 in the Great Lakes. This trend is very similar to Aroclor production history. In the Indiana Harbor Ship Canal, PCBs appear around 1935 and remain at very high levels between 1940 and 1980, probably reflecting the history of use at the nearby steel mill. In contrast, the non-Aroclor PCBs in the Lake Ontario and IHSC sediment cores, including PCB11 and heavily chlorinated congeners PCB206, 207, 208 and 209 reach a peak in the 1950s, decline and peak again in the 1970s or in the early 1980s. All five congeners have been previously measured in commercial paint pigment. PCB11 was found to peak about 5 years later than Σ PCBs, and is probably associated with the production or use history of diarylide yellow pigments. The temporal distribution profiles of these non-Aroclor PCBs are well correlated with the production history of paint pigments and dyes. Although it is well known that the production of Aroclor PCBs is preserved in Great Lakes sediments, this study is the first to show that production of non-Aroclors are also preserved in the sediments as a record of long term trends in environmental exposure.

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Introduction

Polychlorinated biphenyls (PCBs) have been used in an extensive variety of applications including transformer oils, hydraulic fluids, plasticizers, flame retardants, and paints due to their chemical stability, resistance to heat, low flammability, and high dielectric constant (De Voogt and Brinkman, 1989), although the intentional manufacturing of PCBs is now prohibited in the United States and almost all other countries. The current sources of PCBs to the environment are believed to be uncontrolled (i.e., natural) recycling of Aroclor PCBs that were manufactured prior to the production ban in 1979, although some PCBs may be produced from dechlorination of Aroclors or from inadvertent production of PCBs during pigment manufacturing (Hu and Hornbuckle, 2010).

The presence of inadvertently produced PCBs in the environment is difficult to determine. Although PCB congener profiles in environmental samples are often different from original commercial mixtures, this is not necessarily due to non-Aroclor sources but to different partitioning and degradation rates for individual congeners in the environment. Therefore, the current and historical environmental exposures to inadvertent or non-Aroclor PCBs are hard to

determine even though congener-specific analysis has become common practice.

There are very little available data concerning emissions of inadvertent PCBs, and air emissions of inadvertent PCBs as trace by-products are poorly reported or unreported. However, in 2008 the presence 3,3'-dichlorobiphenyl (PCB11) was detected in air (Choi et al., 2008; Hu et al., 2008). Since then it was reported in air of Cleveland, Philadelphia, and several sites around the Great Lakes (Basu et al., 2009; Du et al., 2009; Baek et al., 2010; Persoon et al., 2010). Because PCB11 is not present in commercial Aroclor mixtures, its presence in ambient air suggests that the source of airborne PCB11 is different from current emission sources of Aroclor PCBs. The high concentration of PCB11 in polar regions suggests a global source (Choi et al., 2008).

PCB11 and other congeners are produced inadvertently during pigment production and are found in commercially available paint. Recently we reported that more than 50 PCB congeners besides PCB11 are present in commercial paint pigments purchased in the United States (Hu and Hornbuckle, 2010). The pattern of PCBs was unrelated to Aroclor production and includes many congeners that are highly bioaccumulative, dioxin-like and/or probable carcinogens. We conclude that paint production and use is a probable source of these PCBs in North America.

The significance of these inadvertent PCBs to the environment and human health is still unknown. In recent years, it has been recognized that the impact of PCBs on the environment and biota is usually due to

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the individual congeners of these mixtures, their interaction with themselves and other pollutants (Safe, 1994; Ludewig et al., 2008). As Aroclor-derived PCBs are generally declining in the environment over the time, the relative contribution of inadvertent PCBs to environmental exposure may increase. It is important that the historical and current trends of inadvertent PCBs be discerned. We hypothesize that the source of PCB11 to the environment also delivers other non-Aroclor PCBs, including those that are highly bioaccumulative and probable carcinogens. Therefore, in order to examine the existence, historical trend and source of non-Aroclor PCBs we investigated their sedimentary records along with Aroclor PCBs through analysis of sediment cores from Lake Erie, Lake Ontario and the Indiana Harbor Ship Canal.

Experimental section

Sediment samples

Sediment collection was conducted during August 7–12, 2003, from Lake Erie (LE-15; 42° 31' N, 79° 53' W) and Lake Ontario (LO-60; 43° 34' N, 77° 12' W) aboard the U.S. Environmental Protection Agency *R/V Lake Guardian*. To obtain the sediment cores, a 30 cm × 30 cm × 52 cm sediment box core was used to take undisturbed sediment from the lake bottom. Each box core was then subcored to accurately preserve the sediment layers. Polycarbonate tubes (7.6 cm diameter × 60 cm length) were inserted into the box core sediment and removed under vacuum to ensure a solid undisturbed column of sediment. The Lake Erie and Lake Ontario cores were hydraulically extruded and collected as 33 and 25 sections (~2 cm thickness), respectively.

The Indiana Harbor Ship Canal (IHSC) core sample (41° 39' N, 87° 28' W) was collected on May 8, 2009, aboard the U.S. Environmental Protection Agency *R/V Mudpuppy*. A submersible vibro-coring system was employed, with a PVC tube (length 4.57 m, internal diameter 0.95 m). The core was segmented every 15 cm into 29 slices. After the sediment core was sliced, the segments were homogenized on the ship deck and divided into 3 precleaned amber jars, around 200 g each. The samples were brought to the laboratory and kept refrigerated at 4 °C until extraction and analysis.

The lake sediments were extracted using a Soxhlet apparatus reflux of hexane. The IHSC sediment samples were extracted using accelerated solvent extraction with hexane and acetone (1:1, v/v). Additional details of sediment sampling, sampling extraction and preparation have been described previously for the LE-15 and LO-60 cores (Peck et al., 2006) and for the IHSC core (Martinez, 2010; Martinez et al., 2010).

Reagents

A calibration standard solution with a full suite of 209 PCB congeners was prepared from five PCB congener solutions purchased from Accu-Standard (New Haven, CT, USA). PCB14 (3,5-dichlorobiphenyl), PCB65 (2,3,5,6-tetrachlorobiphenyl), PCB166 (2,3,4,4',5,6-hexachlorobiphenyl) and PCB204 (2,2',3,4,4',5,6,6'-octachlorobiphenyl) were purchased from Cambridge Isotope Laboratories, Inc. (MA, USA). Acetone and hexane (pesticide grade) were purchased from Fisher Scientific (Fair Lawn, NJ, USA).

Sample analysis

The sample extracts were spiked with 100 ng of PCB204 as the internal standard. The resulting solutions were concentrated into 100 µL and transferred into in a 200-µL glass insert contained with a 2-mL amber autosampler vial for the LE-15 and LO-60 samples. The extracts of the IHSC samples were concentrated into 500 µL. All 209 PCB congeners, in 168 chromatographic peaks, were analyzed using a gas chromatograph with mass selective detection (GC-MS/MS) modified from the EPA method 1668A (U.S. EPA, 1999). The quantification of PCB

congeners was carried out by an Agilent 6890N gas chromatograph with an Agilent 7683 series autosampler coupled to a Waters Micromass Quattro micro GC mass spectrometer (Milford, MA, USA) operating under electron impact (EI) positive mode at 70 eV and multiple reaction monitoring (MRM), and the trap current was 200 µA.

Quality assurance/quality control

Every batch included eight to ten samples plus two solvent blanks and a reference standard. The archived samples were preserved in ~1.5 mL hexane, and concentrated to 100 µL prior to analysis. Hexane serving as a solvent blank was processed using the same analytical procedure. No contamination of PCBs was found in solvent blanks. The reference standard was the same as the calibration standard with the known amount of spiked PCBs. The relative standard deviation of detected Σ PCBs and PCB11 was less than 5% between batches. The limits of quantification were between 0.02 and 0.05 ng/congener per sample based on the strength of background signals ($S/N > 3$). Standard Reference Material 1944 was measured, and the results were compared to certified values with the average difference of $15 \pm 8.9\%$.

Results and discussion

Sediment dating

Dating of the Lake Erie core (LE-15) has been described previously (Peck et al., 2006). Briefly, the LE-15 core was divided into 33 sections, and the age for each section was determined from the ^{210}Pb activity using the rapid steady-state mixing model (Peck et al., 2006). The sediment rate was $0.73 \text{ g cm}^{-2} \text{ year}^{-1}$ which is larger than reported values for other locations in the lake because this core was collected from a high-deposition zone. The core contained sediment deposited from 1974 to the sampling year of 2003 which is not long enough to capture the whole PCB record due to the high sediment accumulation rate.

The Lake Ontario core (LO-60) was sectioned into 25 slices at 2-cm intervals, and these sediment samples were initially not dated. For this study, we estimated the age of each segment using deposition rates reported for other cores collected nearby and from the record of Aroclor PCBs in the core. In the same area of the lake, Wong et al. found PCBs peaked in concentration in 1970 with various sedimentation rates in three sampling sites (LO90-E30, LO90-F31 and LO90-G32) which are relatively close to our sampling location (Wong et al., 1995). The distances of these three sites are about 24, 32 and 40 km away from the LO-60 site. We assumed Σ PCBs peaked on the same time in our site (LO-60) to calculate the sedimentation rate ($0.0583 \text{ g cm}^{-2} \text{ year}^{-1}$) which falls in the reported range of 0.0310 to $0.0815 \text{ g cm}^{-2} \text{ year}^{-1}$ in this area (Wong et al., 1995). Based on the calculated sedimentation rate, each archived sediment sample was dated. The average year of the core samples ranged from the sampling year of 2003 to 1700 with the assumption of a constant sedimentation rate during the whole period. Fortunately it is not necessary to accurately determine the sediment ages for the deep bottom sections before 1900.

The Indiana Harbor Ship Canal core (IHSC) core was sliced every 15 cm into 29 sections which were dated using the reported average sedimentation rate of $2.1 \text{ g cm}^{-2} \text{ year}^{-1}$ (Petrovski, 1995). The year of the middle of each core segment ranged from 2007 to 1842 with the assumption of a constant sedimentation rate during the whole period. The PCB data from sediment slices dated before 1920 were much lower in concentration and excluded for analysis for both the IHSC core and the LO-60 core.

Σ PCBs

The profile of each section was statistically analyzed for correlation with commercial Aroclor mixtures including Aroclors 1221, 1016, 1242, 1248, 1260 and 1254 (Frame et al., 1996). Cosine theta metric

($\cos \theta$) was employed to determine similarities between congener profiles. This metric uses the cosine of the angle between two multivariable vectors (the profiles) where a value of -1.0 describes two completely different vectors and 1.0 describes two identical vectors (Davis, 1986; DeCaprio et al., 2005; Magar et al., 2005). The profiles of the topmost section for each core are displayed (Fig. 1). The PCB profiles of LE-15 and LO-60 most resemble Aroclor 1254 (see Tables S1 and S2) while the profile of the IHSC core is more like Aroclor 1248 as previously reported (Martinez, 2010; Martinez et al., 2010).

Commercial production of PCBs in the U.S.A started in 1929, although the production data have been documented only since 1954 (De Voogt and Brinkman, 1989). The Σ PCB vertical distribution profiles in all three sediment cores clearly reflect the known historical production of commercial Aroclors in the North America. The Σ PCB concentrations started to increase around 1930 in agreement with the onset of PCB production. Aroclor production peaked around 1970 when Σ PCB concentrations also peaked in the LO-60 and IHSC cores (Fig. 2). After that, PCB production declined and this is reflected in the PCB concentrations in the sediments. Since 1990s Σ PCB concentrations have been leveling off in sediments. Although the Lake Erie sediment core did not reflect the whole PCB production period, the same trend was observed during the recorded period. The highest accumulation rates for LO-60, LE-15 and IHSC cores were 1.7×10^6 ng m $^{-2}$ year $^{-1}$,

4.6×10^6 ng m $^{-2}$ year $^{-1}$ and 1.9×10^9 ng m $^{-2}$ year $^{-1}$, respectively, around the peak production year of Aroclor mixtures. The high level of Σ PCBs from 1940 to 1980 for the IHSC core is probably due to the constant utilization of Aroclor 1248 in high volume by the local industries until the production was banned. The local use of Aroclors has been previously observed in the sedimentary records (Bzdusek et al., 2005; Li et al., 2005).

The concentration of PCB commercial mixtures is much lower in sediments dated earlier than 1930 in LE-60 and IHSC cores, which is in agreement with the start of PCB production in 1929 in the North America, verifying the determination of sediment ages at least over the period between 1930 and 2003. The presence of some congeners in trace level in sediment prior to the production of PCBs was detected in the LE-60 and IHSC cores. The congeners detected prior to PCB production primarily include PCB11, abundant congeners such as 20/28, 52, 66, 95 and highly chlorinated congeners such as PCBs 206, 207, 208 and 209. This observation has been reported before but it is not totally explained (Sanders et al., 1992; Gevao et al., 1997). The possible causes include bioturbation, smearing during core extrusion and selective diffusion (Gevao et al., 1997). The detection of PCB11 and highly chlorinated congeners beyond the starting time of PCBs production may be additional evidence of their different source from Aroclor PCBs while the presence of the abundant congeners was probably caused by the above described effects.

PCB11

Σ PCB concentrations decreased from the bottom (older) section of the core all the way to the surface in the Lake Erie core (Fig. 2). However, PCB11 remained relatively constant over this period (Fig. 3). The highest accumulation rates for LO-60, LE-15 and IHSC cores were 1170 ng m $^{-2}$ year $^{-1}$, $3,840$ ng m $^{-2}$ year $^{-1}$ and 7.7×10^5 ng m $^{-2}$ year $^{-1}$, respectively. The average PCB11 concentrations in LE-15, LO-60, and IHSC cores are 0.36 , 0.80 and 9.8 ng/g d.w. with the range from 0.011 to 36.9 ng/g d.w. The average fraction of PCB11 relative to Σ PCB is 0.002 in the lake sediment cores and 0.0003 in the IHSC sediment core. The fractions are lower than that in air samples of Korea (0.09 – 0.27) (Baek et al., 2010) and that in Chicago air (0.04) (Hu et al., 2008, 2010). It makes sense that PCB congener distribution is generally skewed toward the heavier chlorinated congeners in sediment, and vice versa in air because of the different physical chemical properties but also the air is reflecting current emissions. If pigments and dyes are a source of PCBs to air, more volatile congeners such as PCB11 will be enriched.

There is no correlation ($R^2 = 0.0003$) between the concentrations of PCB 11 and that of the total PCBs in the core LE-15 (Fig. 4). The Lake Ontario sediment core (LO-60) and the IHSC core also show the weak correlation ($R^2 = 0.50$ and 0.70 , respectively) relative to Σ PCB over a longer period (Fig. 4). However, the other PCB congeners except nona- and deca-congeners and those with a very low detection frequency generally show good correlation ($R^2 > 0.85$) with Σ PCBs (Fig. 4 and Fig. S1). For example, PCB52 and Σ PCBs show a very strong correlation with R^2 values of 0.984 , 0.990 and 0.995 , respectively, in LE-15, LO-60 and IHSC sediment cores (Fig. 4). This suggests that the source of PCB 11 currently present in the sediments is not the same as those of the other PCB congeners.

Previous studies have shown the different sources of PCB11 and Σ PCBs (Choi et al., 2008; Hu et al., 2008; Basu et al., 2009; Du et al., 2009; Hu and Hornbuckle, 2010; Rodenburg et al., 2010); however, the specific source of PCB11 in sediments is still not clear. Litten et al. (2002) detected PCB11 in surface waters and effluent waste streams associated with pigment manufacture in 2002. PCB11 was detected in air at several different locations in 2008 and 2009 (Hu et al., 2008; Basu et al., 2009; Du et al., 2009; Hu et al., 2010). Basu et al. (2009) found that PCB11 source(s) are associated with human or industrial activities with a good correlation between PCB levels and surrounding human population. Previous work in our laboratory revealed a link

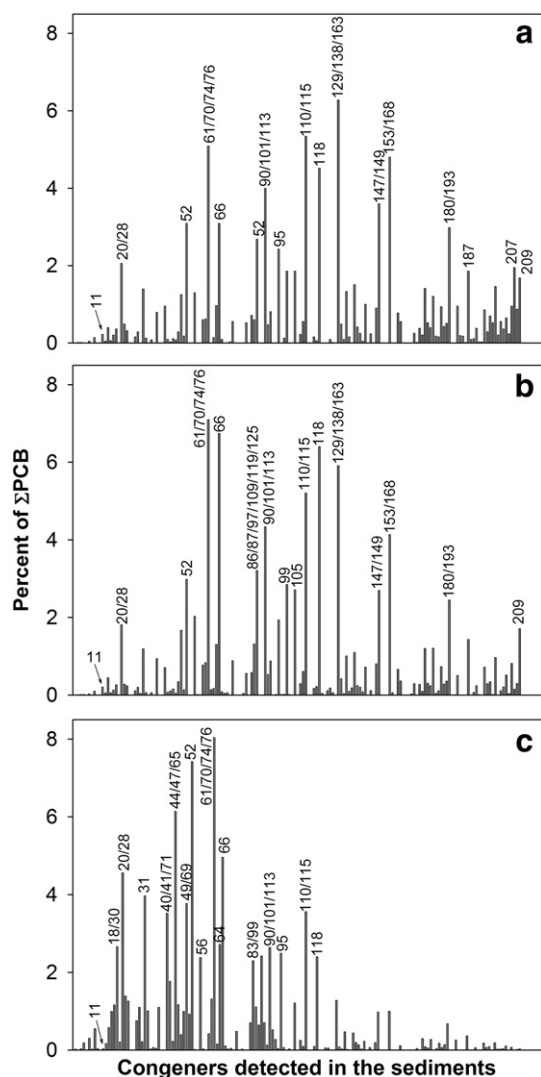


Fig. 1. PCB profiles of the topmost sections of cores (a) LO-15, (b) LO-60 and (c) IHSC. Congeners are ordered by IUPAC number and the list is provided in the Supporting Information, Fig. S1.

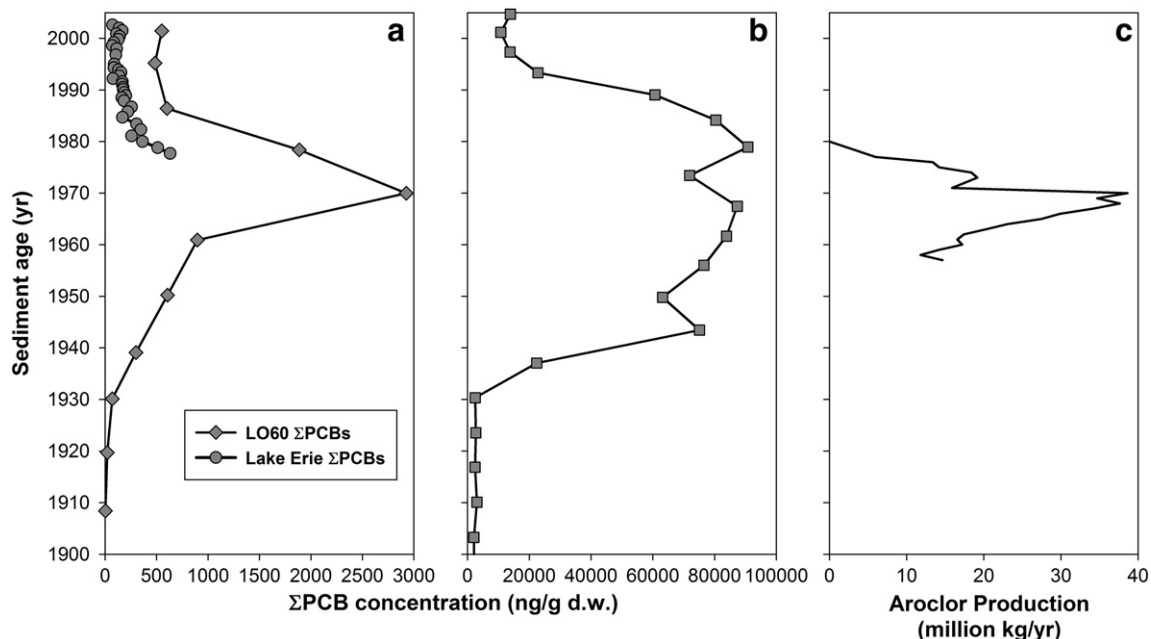


Fig. 2. Σ PCB concentration trends in sediment from (a) Lake Erie and Lake Ontario, and (b) Indiana Harbor ship canal, reflect production and use of commercial Aroclor mixtures in North America (c).

between PCB11 with the production of pigments/dyes by measuring PCB congeners in commercial pigments (Hu and Hornbuckle, 2010), and PCB11 was the most frequently detected one although there are more than 50 congeners present. More recently, Baek et al. suggested that the source of PCB11 is located in residential areas rather than in industrial and semirural areas (Baek et al., 2010). They also suggested that it is probably the building materials or the decoration and furnishings of the buildings. All these pieces of evidence suggest that pigments/dyes are probably the source of PCB11 in the environment.

PCB11 peaked in concentration about 5 years after Σ PCB in 1970 (Fig. 2 and Fig. 3). The different peak times also indicate PCB11 and Σ PCB have different sources. The spikes and trends of PCB11

concentrations are well correlated with pigments/dyes production in the United States (Fig. 3) as Σ PCB concentrations correspond to PCB production (Fig. 2). This supports the hypothesis proposed in our previous studies (Hu et al., 2008; Hu and Hornbuckle, 2010). There are two possible mechanisms of PCB11 formation in pigments/dyes. First, PCB11 is unintentionally produced as by-products in azo and phthalocyanine pigments/dyes when di- or tri-chlorobenzene is used as a reaction solvent medium during the manufacturing process (Hu and Hornbuckle, 2010). Second, PCB11 is formed as a degradation product from a particular azo pigment/dye: diarylide yellow. PCB11 has been reported as a degradation product from diarylide pigments at the elevated temperature of over 200 °C (Az et al., 1991), while it is still

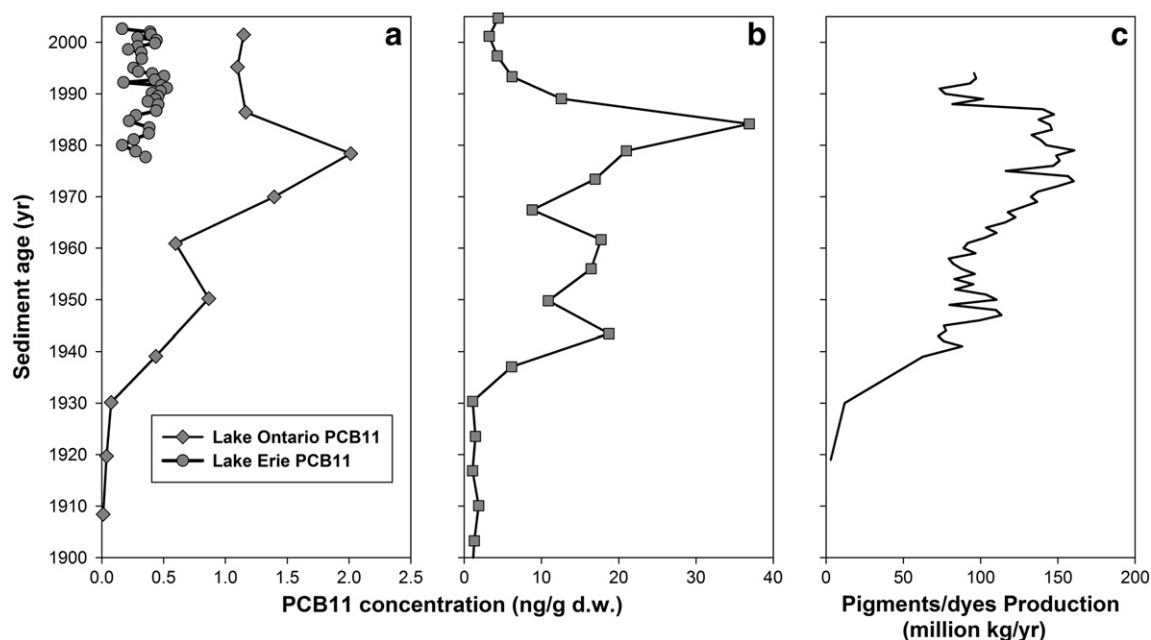


Fig. 3. PCB11 concentration trends in sediment from (a) Lake Erie and Lake Ontario, and (b) Indiana Harbor ship canal, reflect the production history of pigments/dyes production in the United States (c).

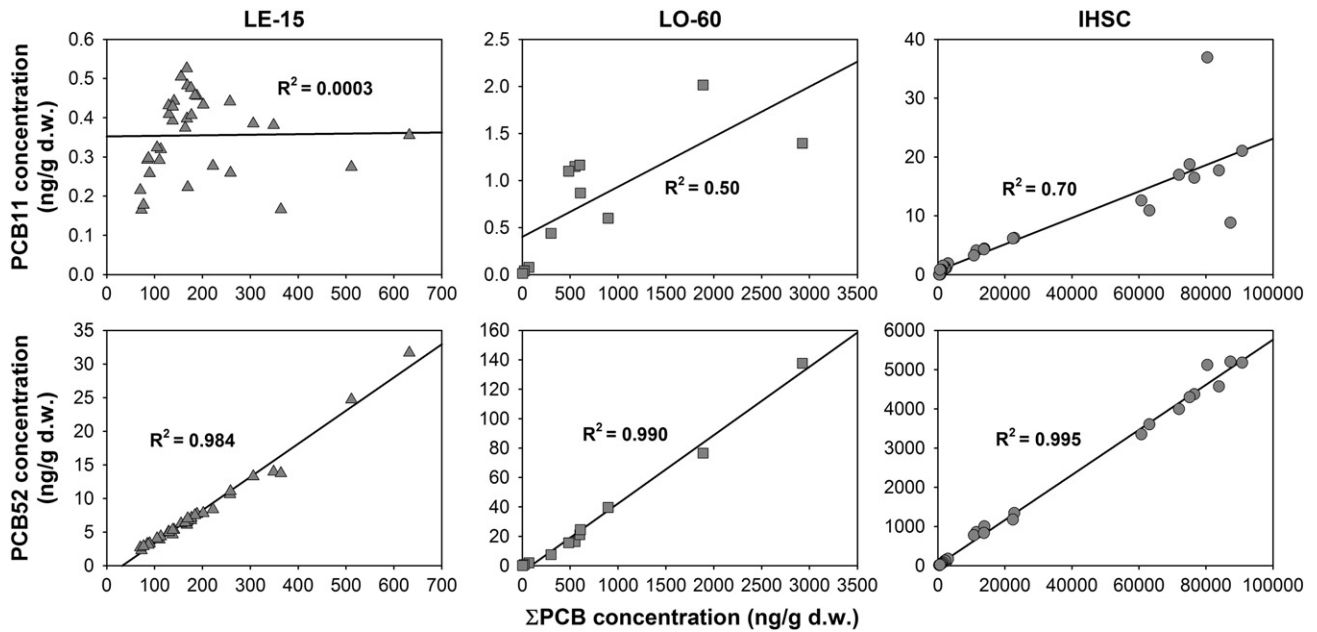


Fig. 4. PCB11 (top row plots) is poorly correlated with Σ PCBs compared to other congeners (e.g., PCB52, bottom row plots) in sediment core samples collected in Lake Erie (left column plots), Lake Ontario (middle column plots) and in IHSC (right column plots).

unknown if this process could happen under environmental conditions. Probably both mechanisms contribute to the environmental release of PCB11.

Other non-aroclor congeners

Most commercial uses of PCBs were in the form of the Aroclor mixtures. However, about 80 individual congeners are commercially available. Upon request any congener can be synthesized with a purity of more than 99% (De Voogt and Brinkman, 1989) and there have been industrial uses of some congeners. For example, PCB209 was produced for use in investment casting waxes in the mid-1970s (Erickson, 1985). In addition, many chemical processes involving carbon, chlorine, and elevated temperatures or catalysts may produce non-Aroclor congeners (U.S. EPA, 2010). However, there are no reports of extensive use or production of any individual congeners since the 1930s.

In addition to PCB11, several highly chlorinated PCB congeners exhibit trends that do not match the Aroclor production data. These congeners were very minor components of Aroclors but were found in the sediments (Table S3). PCBs 206, 207, 208 and 209 showed weak correlation with Σ PCB in all three sediment cores except PCB206 in the Lake Erie core (Table 1). PCB206 is present in Aroclor 1260 and Aroclor 1254 (Frame et al., 1996), which might make PCB206 more correlated with the Aroclor production in the Lake Erie core. The fully chlorinated PCB209 and the nonachlorobiphenyls are present in phthalocyanine green pigments (Hu and Hornbuckle, 2010). PCB209 is also suspected to be associated with production of titanium dioxide. During the purification of titanium dioxide a carbon-chlorination process may produce heavily chlorinated congeners (Rowe et al., 2007). PCB 209 was also detected as a significant fraction of Σ PCB in

sediments, suspended solids, and fish in the Delaware River and Bay and the upper Chesapeake Bay (Rowe et al., 2007; Du et al., 2008). The investigators also noticed that nonachlorobiphenyl congeners were also unusually enriched in their samples.

PCB11 and the nona- and deca-chlorinated congeners exhibit accumulation trends in Lake Ontario that are similar to the national production trends of pigments and dyes (Fig. 5). The different peak years of accumulation for the different congeners, particularly between PCB11 and the highly chlorinated congeners, may be due to the different regional or national production history of their associated pigments/dyes. For example, PCB11 is associated with diarylide yellow pigments while nona- and deca-chlorinated PCBs are linked with phthalocyanine green pigments and titanium dioxide white pigments (Hu and Hornbuckle, 2010). We did not observe this

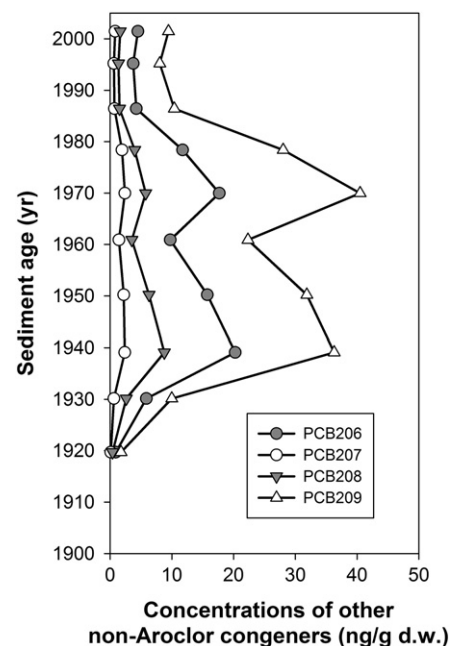


Fig. 5. The historical trends for nona- and deca-chlorobiphenyl congeners in LO-60.

Table 1
Correlation coefficients (R^2) of select non-Aroclor congeners with Σ PCBs.

	LE-15	LO-60	IHSC
PCB11	0.0003	0.50	0.70
PCB206	0.95	0.34	0.27
PCB207	0.065	0.39	0.0008
PCB208	0.77	0.19	0.36
PCB209	0.69	0.47	0.50

phenomenon in the Lake Erie core because our dataset is truncated. We did not observe this phenomenon in IHSC because the harbor system has a very small watershed that is intensely affected by local industries. In fact, most of the water flow in the IHSC consists of wastewater or cooling water discharge. The accumulation pattern of non-Aroclor congeners in IHSC sediments probably reflects their use by local industries rather than regional or national production and use patterns.

Conclusions

This study provides evidence that inadvertent generation of non-Aroclor PCBs results in environmental exposures to these congeners. In particular, we have shown characteristic peaks in concentration of non-Aroclor PCBs, their weak temporal correlation with Σ PCBs and their different temporal trends in the open lake and canal. The production of pigments and dyes matches the accumulation of inadvertently produced PCBs while Σ PCB concentration trends reflect manufacture and use of commercial Aroclor mixtures. It is the first time to show that production of non-Aroclors are preserved in the sediments as a record of long term trends in environmental exposure.

Important questions remain about PCB congeners that have sources from more than one activity. For example, although we have previously shown that currently available commercial paint pigments contain many PCBs, including dioxin-like congeners, we are unable to use sediment records to quantify the sources of any congeners that were also produced and distributed in Aroclor mixtures. We cannot distinguish the historical Aroclor source from current (and legal) sources of most of the non-Aroclor congeners, which are potentially hazardous. These non-Aroclor congeners are overshadowed if they are abundantly present in commercial PCB mixtures but low in the unrecognized source(s).

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